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THE ATOMIC STRUCTURES OF THE Au-INDUCED RECONSTRUCTIONS

OF Si(111): 5×1, √3× √3 AND 6×6

by

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The Au-induced Si(111) reconstructions were examined using LEED and ICISS. The Au atoms in all three structures are bonded in threefold hollow sites 2.0 ± 0.2Å above a bulk-like Si(111) surface. For coverages up to 0.4 monolayer, the Au forms rows along $[\bar{1}10]$-type azimuths (5×1 phase). At coverages up to ~0.9 monolayer, a honeycomb is formed with some centered adatoms 0.3 ± 0.05Å below the Au hexagons ($\sqrt{3}\times\sqrt{3}$ structure). For a coverage of ~1.0 monolayer, the surface is a 75:25 mixture of filled and empty Au hexagons in a 6×6 superstructure.

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The Atomic Structures of the Au-Induced Reconstructions

of Si(111): 5×1, $\sqrt{3}\times\sqrt{3}$, and 6×6

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The Au-induced Si(111) reconstructions have been examined using
LEED and ICISS. The Au atoms in all three structures are bonded in
threefold hollow sites ~2.0Å above a bulk-like Si(111) surface. For
Au coverages up to 0.4 monolayer, the adatoms form rows along $[\bar{1}10]$-
type azimuths (5×1 phase). At coverages up to ~0.9 monolayer, a
honeycomb framework is formed with additional adatoms 0.3Å below the
honeycomb plane in the center of some of the Au hexagons ($\sqrt{3}\times\sqrt{3}$
structure). For a coverage of ~1.0 monolayer, the surface is a 75:25
mixture of filled and empty Au hexagons in a 6×6 superstructure.

The structure determination of metal-semiconductor interfaces has been of paramount interest both for practical and fundamental reasons. The Au/Si(111) system, which has been studied extensively using many different surface-sensitive techniques, reconstructs into 5×1, $\sqrt{3}\times\sqrt{3}$, and 6×6 structures, depending on the amount of gold deposited and the annealing condition.[1-8] These surfaces have received a great deal of attention over the years, but as yet there is no consensus about the atomic structures of the three observed reconstructions. One of the major points of interest is whether the Au atoms penetrate the Si surface layer and/or form an interfacial silicide phase and, if so, at which coverage of Au this crossing of the surface plane occurs. Auger peak intensity versus surface coverage plots for Au on Si(111) show a definite decrease in slope at the transition from the $\sqrt{3}\times\sqrt{3}$ to the 6×6 reconstructions, and this has been interpreted as being caused by Au-Si compound formation.[3,4] On the other hand, a study of Low-Energy Electron Diffraction (LEED) spot profiles indicated that the transition from the $\sqrt{3}\times\sqrt{3}$ to the 6×6 phases is gradual and that the two reconstructions are closely related.[8] Thus, further studies using a highly surface-sensitive and mass-selective probe of local atomic geometry, i.e., ion scattering, were required to resolve this issue. The aim of this investigation was to determine the atomic structures of the three reconstructions and understand how they are related to one another. This study further illustrates the capabilities of Impact Collision Ion Scattering Spectroscopy (ICISS)[9,10] for obtaining surface structure information in real space.

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Mirror-smooth Si(111) wafers (5×10×0.3 mm) were used as the substrates in this study. The surface of each specimen was cleaned in the UHV scattering chamber by annealing at 450°C for 15 mins. and flash heated to about 1000°C for 3 secs to obtain a sharp 7×7 LEED pattern. The level of surface contamination was below the detection limit of Auger spectroscopy. The surfaces were prepared by evaporating Au onto a room-temperature (RT) substrate by heating a Au wire wrapped around a tungsten filament. The rate of deposition, which was measured by an Inficon XTM thin film monitor, was approximately 0.1 monolayer (ML) per minute. The sample was annealed by heating resistively at about 700°C for 10 mins. Surfaces with approximately 0.40 ML, 0.80 ML, and 1.10 ML of Au were prepared on different Si(111)7×7 substrates to produce 5×1, $\sqrt{3}\times\sqrt{3}$, and 6×6 LEED patterns, respectively. The domain sizes of the resulting surfaces were characterized by measurement of LEED spot profiles (Fig.1), which contained the sharpest spots for the above coverages.

The LEED patterns observed for these three structures were strong and sharp with low background. Details of the data collection and LEED I-V spectra have been presented elsewhere.[11,12] The I-V curves are quite similar for the integral order spots of all three surfaces, which indicates that they are all structurally related. Fig.1 presents the LEED spot profiles as the screen intensity versus relative momentum transfer (Å^{-1}). From the spot widths, the characteristic length scale of the domains producing the fractional LEED spots was determined to be approximately 420 Å, 340 Å, and 610 Å for the 5×1, $\sqrt{3}\times\sqrt{3}$, and 6×6 structures, respectively.

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The ion scattering experiments were performed using 5-keV lithium ions as projectiles in order to avoid the difficulties associated with neutralization of noble gas ions. The ion scattering experiments were performed in a UHV chamber coupled to a 30-keV ion accelerator with a Colutron ion source.[10] ICISS polar scans were measured by detecting the intensity of 5-keV Li^+ that had scattered elastically from Au atoms into an electrostatic analyzer at a 157° scattering angle. The data shown in Fig.2 were collected as a function of the ion beam incidence angle with respect to the sample surface along two perpendicular azimuthal orientations, namely the $[11\overline{2}]$ and $[\overline{1}10]$, which had ICISS angular distributions essentially identical to those of the $[\overline{1}\overline{1}2]$ and $[1\overline{1}0]$ azimuths, respectively. Ion-bombardment damage to the surfaces was not observed for the Li^+ doses required to accumulate the ICISS scans, which were very reproducible.

The ICISS data from all three surfaces are remarkably similar, considering the drastically different LEED patterns characteristic of each reconstruction. The polar scans along the $[11\overline{2}]$ azimuth are essentially identical in shape for the $\sqrt{3}\times\sqrt{3}$ and 6×6 structures, with the maximum of the surface flux peak for the 5×1 surface at a slightly lower polar angle. For the $[\overline{1}10]$ azimuth, the primary difference is that the shoulder on the surface flux peak becomes more prominent and moves to higher polar angle with increasing Au coverage. These similarities indicate that the local atomic structures of all three reconstructions are related, and that the reconstructions appear to evolve smoothly as the surface Au concentration varies. The principal dissimilarities among the structures are apparently in their long-range ordering.

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The absence of intensity modulations in the ICISS yield at high polar angles (the data were collected out to 90°) indicated that the Au atoms on all three surfaces were confined to a single plane at the surface. The ICISS angular scans in Fig.2 differ markedly from those for the Li^+ scattering from Ni atoms at the $NiSi_2(001)$ surface. For that case, the surface layer was a Si plane, and there was considerable modulation of the ICISS yield from Ni at higher polar angles.[10] Thus, all the flux peaks in the ICISS polar scans of Fig.2 resulted from Au atom pairs above the Si(111) surface when Au atoms were exposed to ion projectiles by passing through the shadow cones[9] cast by neighboring Au atoms.

The solid lines in Fig.2 are the result of computer simulations[11,13] based on a scattering probability calculation[14] introduced by Oen[15] and further developed by Tromp and van der Veen.[15] The scattering was represented as the sum of encounters with an array of diatomic molecules, and was calculated by determining the probability density that an ion incident along a certain direction could hit each target atom in the model structure. The results of the individual two-atom calculations were then combined together in the proper fashion to simulate the atomic arrangement of a particular surface-structure model and scattering geometry.

The experimental ICISS data have been compared with computer simulations for all the models that have been proposed for the Au or Ag on Si(111) surfaces.[11-13] On the basis of these comparisons, any model placing Au atoms below the Si surface can be rejected, and only the models discussed below demonstrated quantitative agreement with the experimental data. For the 5×1 structure, the calculations

(Figs.2a and 2b)[11] were based on a structural model consisting of three equivalent domains with strings of Au atoms along the $[\bar{1}10]$-type azimuths (Fig.3).[1] The best agreement for the $\sqrt{3}\times\sqrt{3}$ surface (Figs.2c and 2d), was obtained for a model that consisted of 70% honeycomb units (the simple honeycomb structure is also shown in Fig.3), and 30% centered-hexagon units in which the adatom at the center of the Au hexagon was 0.3Å below the honeycomb plane.[12,13] For the 6×6 structure, a model with 20% of the honeycomb and 80% of the centered-hexagon units gave the best fit to the data (Figs.2e and 2f).[12,13] Since the scattering features along the $[11\bar{2}]$ and $[\bar{1}\bar{1}2]$ azimuths were essentially identical, the Au atoms are most likely to be located at high symmetry sites above the Si(111) surface. In all three structures, by comparing the ICISS data for Li^+ scattering from Si atoms to computer simulations,[12,13] Au was shown to occupy threefold hollow sites approximately 2.0Å above an essentially bulk-like Si(111) surface.

In order to construct meaningful models of the Au on Si(111) surfaces, the long-range order implied by the LEED patterns must be reconciled with the short-range order determined by ICISS. For the 5×1 surface, the model shown in Fig.3 was originally proposed on the basis of the LEED pattern and the maximum surface coverage that displayed only the 5×1 pattern. The same model also provided an excellent quantitative description of the ICISS data, and is therefore almost certainly correct. Of all the existing models, the simple honeycomb structure agreed most closely with the experimental data for the $\sqrt{3}\times\sqrt{3}$ structure, but an even better agreement was found for a mixture of honeycomb and centered-hexagon units. Figure 3 compares

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the simple honeycomb structure to a particular 5×1 domain, and the similarities between the two structures are evident. Because of the larger distance between atoms along the [11$\overline{2}$] azimuth in two of the three domains, the ICISS surface flux peak appeared at a lower polar angle along this azimuth for the 5×1 surface. However, it is not possible to obtain a simple honeycomb simply by adding more atoms to the 5×1 row structure; some of the atoms in the [$\overline{1}$10]-like rows must be removed to obtain the empty site at the center of the Au hexagons. Apparently, the energy difference between an empty and a filled hexagon is small, so that on a real surface both are found.[17] Both units form a basis for a $\sqrt{3}×\sqrt{3}$ diffraction pattern, so that is the symmetry observed in LEED.

As the Au coverage increases further, the additional adatoms go into the centers of the remaining unfilled hexagons, until a stable 6×6 structure is formed. Since these Au atoms are located below the honeycomb plane, the detected Auger yield from the centered atoms may be less than that for the honeycomb atoms, which could explain the break in the Auger yield vs. coverage curves.[1,4] A sensible 6×6 structure may be constructed from 25% of the honeycomb and 75% of the centered-hexagon units, as shown in Fig.4, which is a combination very close to that determined from the ICISS data.[12] While the $\sqrt{3}×\sqrt{3}$ structure displayed almost the same ion scattering features (Figs.2c and 2d) as those for the 6×6 structure (Figs.2e and 2f), the LEED spot profiles indicated that the $\sqrt{3}×\sqrt{3}$ surface was not as ordered as the 5×1 or 6×6 surfaces; the areas of the ordered domains are approximately in the ratio 3:2:6 for the 5×1, $\sqrt{3}×\sqrt{3}$, and 6×6, respectively. These findings suggest that the $\sqrt{3}×\sqrt{3}$ surface is not a pure phase but

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a transitional structure between the 5×1 and the 6×6 phases. The $\sqrt{3}\times\sqrt{3}$ surface has a higher concentration of empty hexagons than the ideal 6×6 superstructure, and the two structural units do not have long-range coherence.

This work demonstrated the unique capabilities of ICISS as a tool for understanding surface structures in real space. The data clearly show that Au atoms do not penetrate the Si(111) surface for any of the three reconstructions. The atomic structures proposed for the three surfaces explain the ICISS and LEED data obtained in this study for the Si(111)-Au-5×1, $-\sqrt{3}\times\sqrt{3}$, and -6×6 reconstructions, and are in excellent agreement with the trends predicted theoretically by Julg and Allouche[17] for the structures that should be formed as a function of increasing Ag coverage on the Si(111) surface. The $\sqrt{3}\times\sqrt{3}$ reconstruction appears to be a transitional phase or incomplete 6×6 structure, as proposed by Higashiyama, et al.[8]

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FIGURE CAPTIONS

FIG.1 - LEED spot profiles for the Si(111)-5×1-Au (a) , - $\sqrt{3} \times \sqrt{3}$-Au (b), and -6×6-Au (c), at normal beam incidence. The ordinate is a relative momentum transfer, expressed in $Å^{-1}$. Note that the momentum scale and the azimuthal orientation, i.e., [$\bar{1}$10] vs. [11$\bar{2}$] of the center profile ($\sqrt{3} \times \sqrt{3}$) are different from the other two profiles.

FIG.2 - Experimental ICISS polar scans (open circles) for 5 keV Li$^+$ scattered at 157° from the Si(111)-5×1-Au (a and b),- $\sqrt{3} \times \sqrt{3}$-Au (c and d), and -6×6-Au (e and f) along the [11$\bar{2}$] and [$\bar{1}$10] azimuths. The solid lines are the result of the calculations for the models described in the text. The intensity scales are for the calculated distributions, which were normalized to the experimental data at a polar angle of 90˙.

FIG.3 - Top view of the Si(111)-5×1-Au and simple honeycomb structures. The surface atomic planes consist of the first Si layer (open circles with cross hatches), the second Si layer (open circles), and the Au overlayer (filled circles).
The upper portion illustrates one of the three rotationally equivalent 5×1-Au (0.4 ML) domains. The lower portion is a simple honeycomb arrangement, in the which the [$\bar{1}$10] rows of atoms are in registry with the 5×1 structure. In the actual $\sqrt{3} \times \sqrt{3}$ structure, some of the Au hexagons have a central

adatom, which sits slightly below (0.3Å) the honeycomb plane.
The 5×1 and √3×√3 unit cells are indicated by dashed lines.

FIG.4- Top view of the Si(111)-6×6-Au surface, in which 75% of the
        hexagons are filled with Au atoms 0.3Å below the honeycomb
        plane (solid circles with inscribed triangles) and ordered in
        a regular superstructure. The stars denote the centers of
        empty hexagons, and the unit cell is indicated by dashed
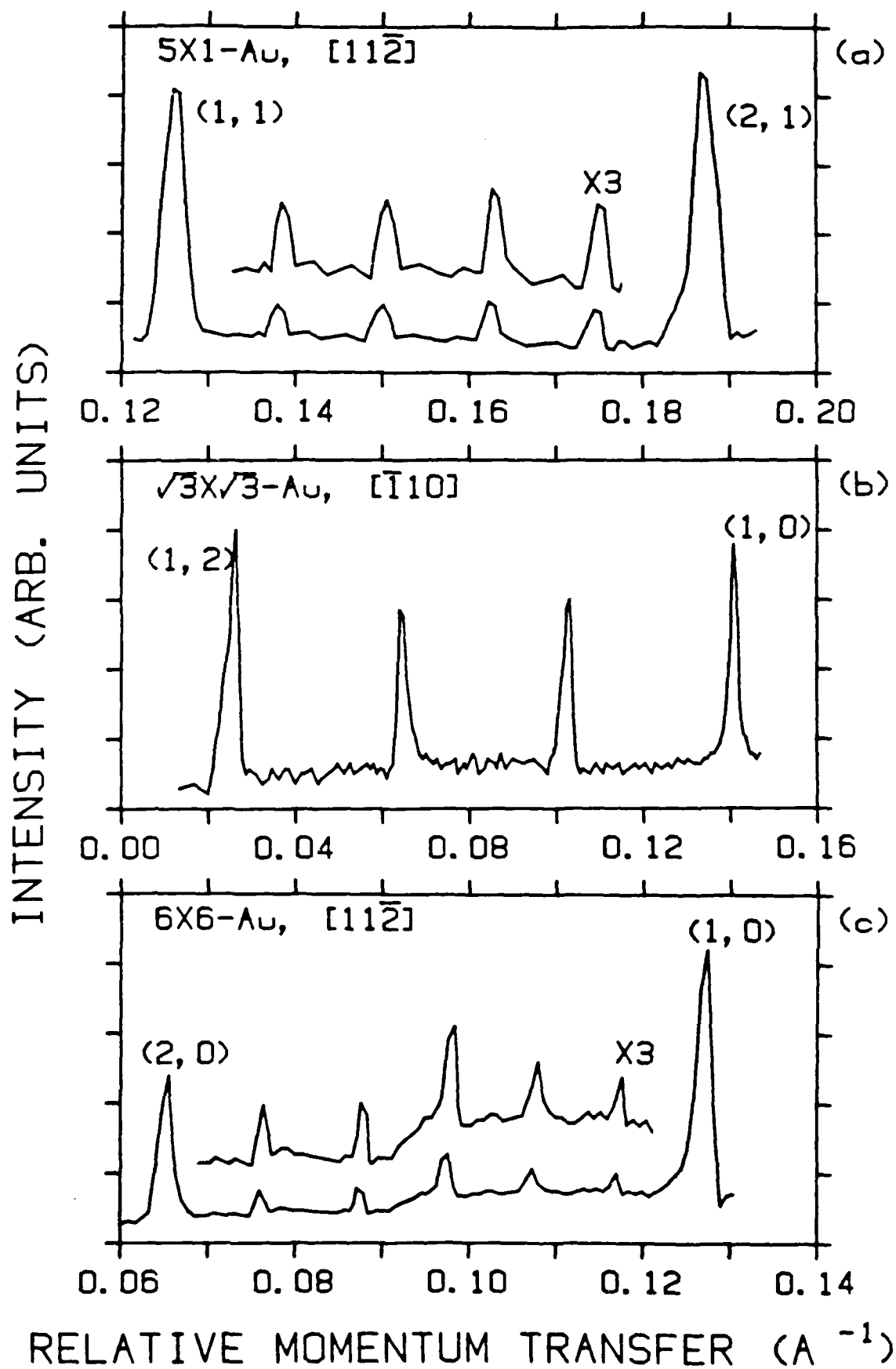   lines. The remaining symbols are the same as for Fig.3.
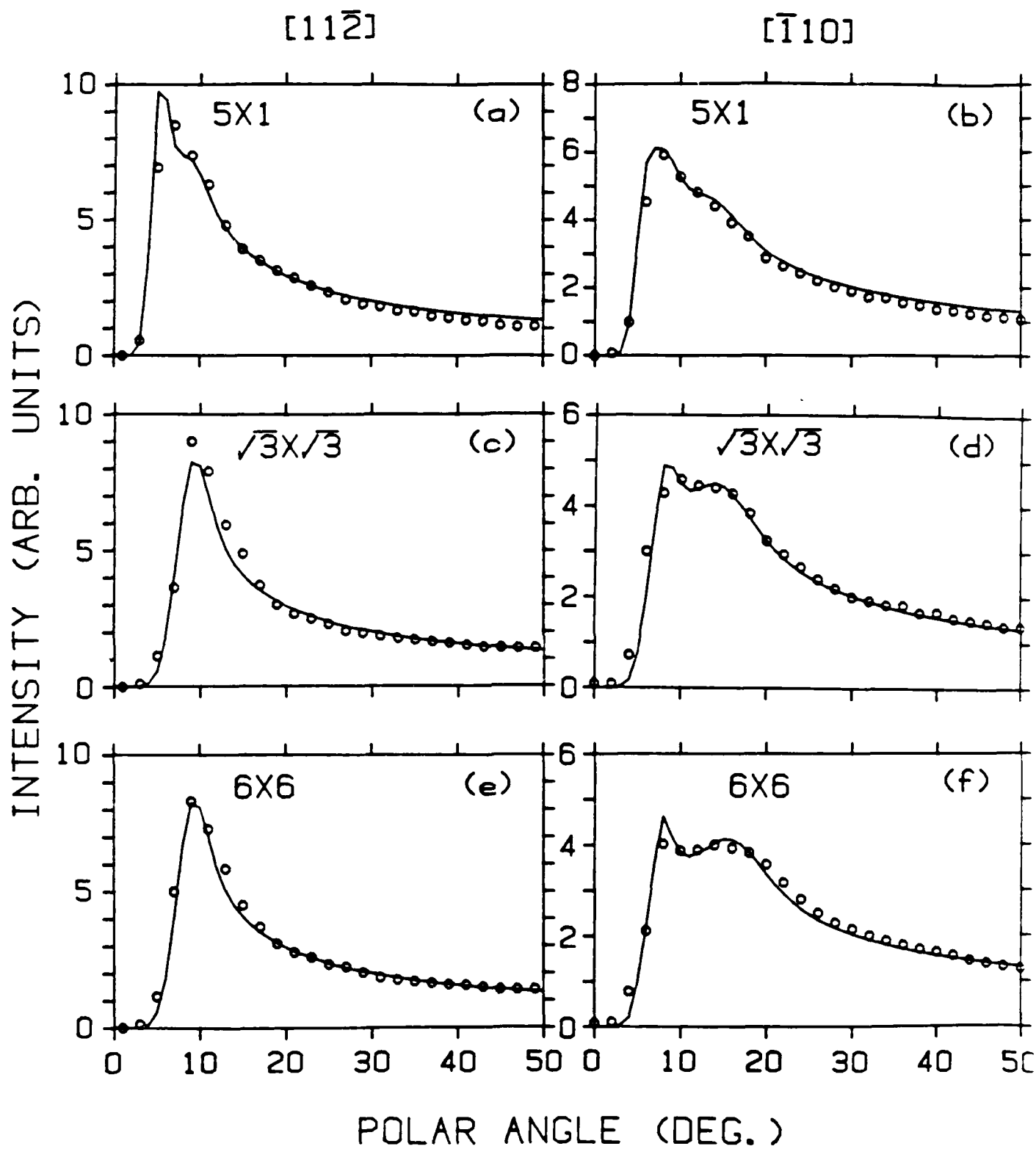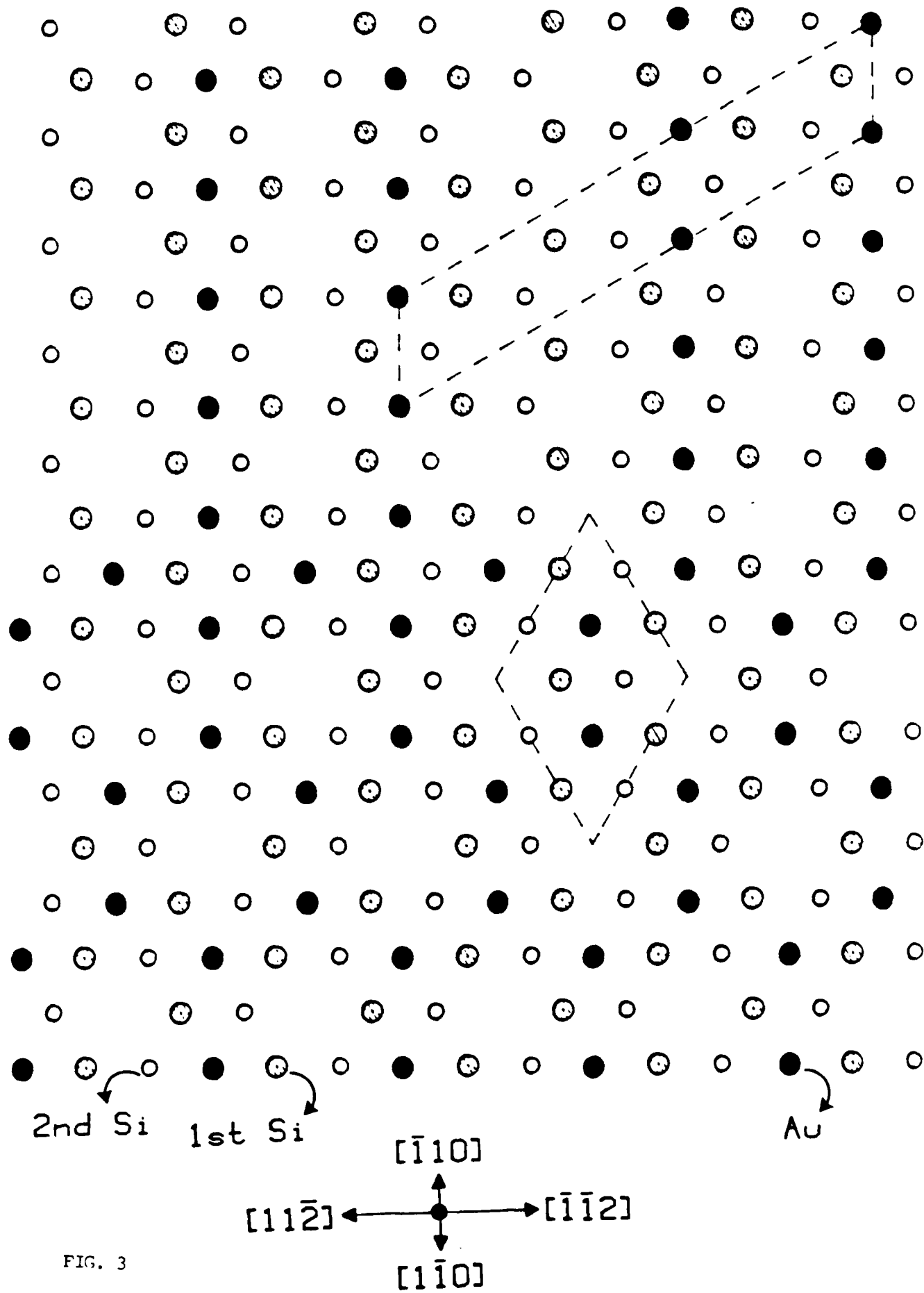
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FIG. 1

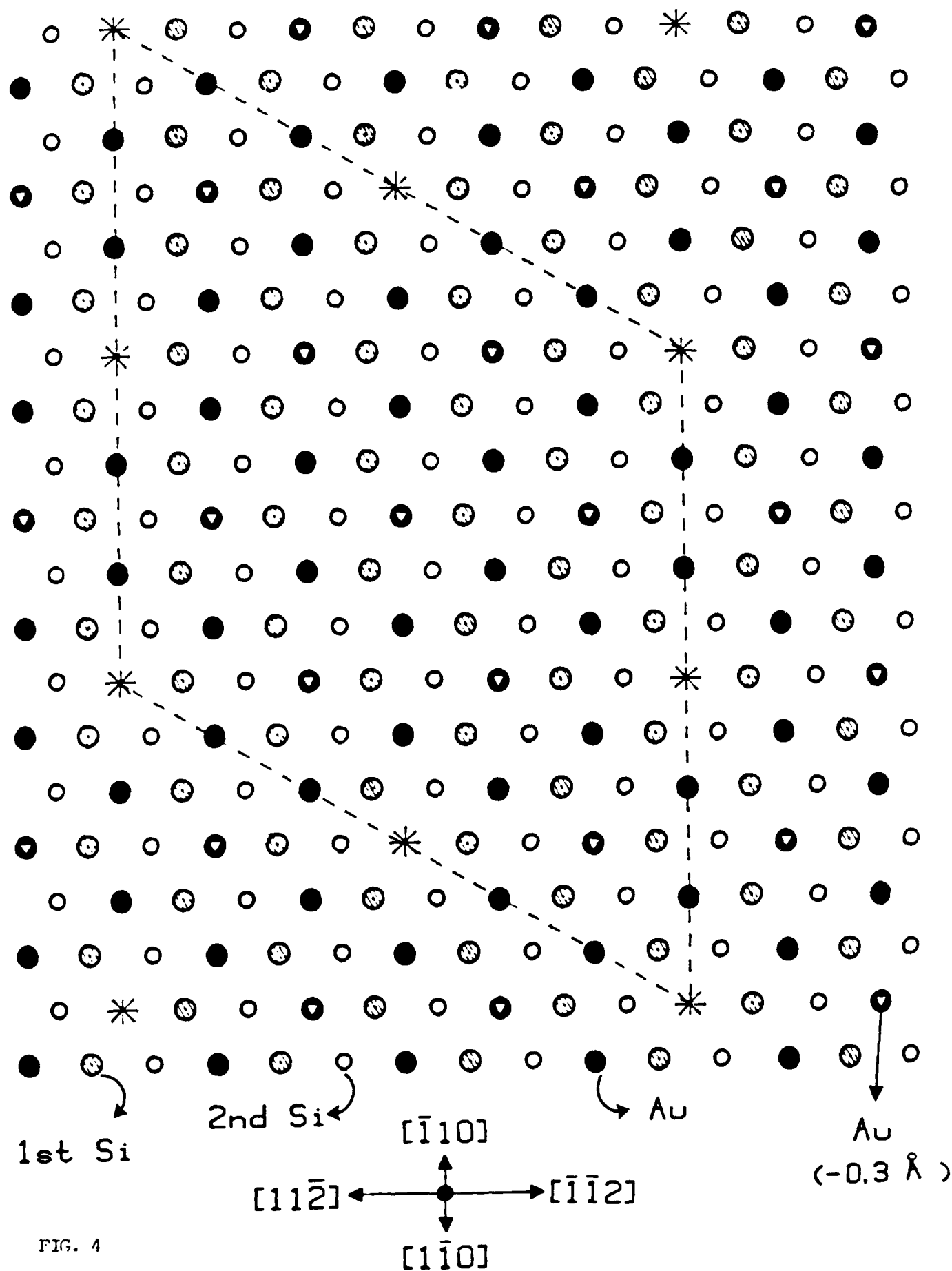FIG. 2

2nd Si   1st Si   Au

$[\bar{1}10]$

$[11\bar{2}] \longleftrightarrow [\bar{1}\bar{1}2]$

$[1\bar{1}0]$

FIG. 3

1st Si

2nd Si

Au

Au
(-0.3 Å)

[Ī10]

[11Ī2]   [ĪĪ2]

[1Ī0]

FIG. 4